

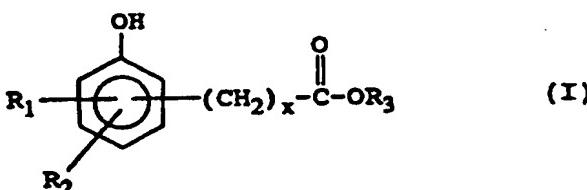
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(54) Title: POLYALKYL HYDROXYAROMATIC ESTERS AND FUEL COMPOSITIONS CONTAINING THE SAME		
(57) Abstract		
Polyalkyl hydroxyaromatic esters having formula (I) or a fuel-soluble salt thereof, where R ₁ and R ₂ are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R ₃ is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5000; and x is an integer from 0 to 10. The polyalkyl hydroxyaromatic esters of formula (I) are useful as fuel additives for the prevention and control of engine deposits.		
 <p style="text-align: right;">(I)</p>		

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01 POLYALKYL HYDROXYAROMATIC ESTERS
02 AND FUEL COMPOSITIONS CONTAINING THE SAME
03

04 BACKGROUND OF THE INVENTION
05

06 Field of the Invention
07

08 This invention relates to novel hydroxyaromatic compounds.
09 More particularly, this invention relates to novel polyalkyl
10 hydroxyaromatic esters and their use in fuel compositions to
11 prevent and control engine deposits.

12 Description of the Related Art
13

14 It is well known that automobile engines tend to form
15 deposits on the surface of engine components, such as
16 carburetor ports, throttle bodies, fuel injectors, intake
17 ports and intake valves, due to the oxidation and
18 polymerization of hydrocarbon fuel. These deposits, even
19 when present in relatively minor amounts, often cause
20 noticeable driveability problems, such as stalling and poor
21 acceleration. Moreover, engine deposits can significantly
22 increase an automobile's fuel consumption and production of
23 exhaust pollutants. Therefore, the development of effective
24 fuel detergents or "deposit control" additives to prevent or
25 control such deposits is of considerable importance and
26 numerous such materials are known in the art.

27
28
29 For example, aliphatic hydrocarbon-substituted phenols are
30 known to reduce engine deposits when used in fuel
31 compositions. U.S. Patent No. 3,849,085, issued
32 November 19, 1974 to Kreuz et al., discloses a motor fuel
33 composition comprising a mixture of hydrocarbons in the
34 gasoline boiling range containing about 0.01 to 0.25 volume

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01 percent of a high molecular weight aliphatic
02 hydrocarbon-substituted phenol in which the aliphatic
03 hydrocarbon radical has an average molecular weight in the
04 range of about 500 to 3,500. This patent teaches that
05 gasoline compositions containing minor amounts of an
06 aliphatic hydrocarbon-substituted phenol not only prevent or
07 inhibit the formation of intake valve and port deposits in a
08 gasoline engine, but also enhance the performance of the
09 fuel composition in engines designed to operate at higher
10 operating temperatures with a minimum of decomposition and
11 deposit formation in the manifold of the engine.
12
13 Similarly, U.S. Patent No. 4,134,846, issued January 16,
14 1979 to Machleder et al., discloses a fuel additive
15 composition comprising a mixture of (1) the reaction product
16 of an aliphatic hydrocarbon-substituted phenol,
17 epichlorohydrin and a primary or secondary mono- or
18 polyamine, and (2) a polyalkylene phenol. This patent
19 teaches that such compositions show excellent carburetor,
20 induction system and combustion chamber detergency and, in
21 addition, provide effective rust inhibition when used in
22 hydrocarbon fuels at low concentrations.
23
24 Amino phenols are also known to function as
25 detergents/dispersants, antioxidants and anti-corrosion
26 agents when used in fuel compositions. U.S. Patent
27 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
28 example, discloses amino phenols having at least one
29 substantially saturated hydrocarbon-based substituent of at
30 least 30 carbon atoms. The amino phenols of this patent are
31 taught to impart useful and desirable properties to
32 oil-based lubricants and normally liquid fuels.
33
34

-3-

01 Nitro phenols have also been employed as fuel additives.
02 For example, U.S. Patent No. 4,347,148, issued August 31,
03 1982 to K. E. Davis, discloses nitro phenols containing at
04 least one aliphatic substituent having at least about 40
05 carbon atoms. The nitro phenols of this patent are taught
06 to be useful as detergents, dispersants, antioxidants and
07 demulsifiers for lubricating oil and fuel compositions.
08
09 In addition, U.S. Patent No. 4,231,759, issued November 4,
10 1980 to Udelhofen et al., discloses a fuel additive
11 composition comprising the Mannich condensation product of
12 (1) a high molecular weight alkyl-substituted
13 hydroxyaromatic compound wherein the alkyl group has a
14 number average molecular weight of about 600 to about 3,000,
15 (2) an amine and (3) an aldehyde. This patent teaches that
16 such Mannich condensation products provide carburetor
17 cleanliness when employed alone, and intake valve
18 cleanliness when employed in combination with a hydrocarbon
19 carrier fluid.
20
21 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz
22 et al., discloses fuel compositions containing (1) one or
23 more polybutyl or polyisobutyl alcohols wherein the
24 polybutyl or polyisobutyl group has a number average
25 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
26 of the polybutyl or polyisobutyl alcohol, or (3) a
27 carboxylate ester of the polybutyl or polyisobutyl alcohol.
28 This patent further teaches that when the fuel composition
29 contains an ester of a polybutyl or polyisobutyl alcohol,
30 the ester-forming acid group may be derived from saturated
31 or unsaturated, aliphatic or aromatic, acyclic or cyclic
32 mono- or polycarboxylic acids.
33
34

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01 U.S. Patent No. 3,285,855, issued November 15, 1966 to
02 Dexter et al., discloses alkyl esters of dialkyl
03 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the
04 ester moiety contains from 6 to 30 carbon atoms. This
05 patent teaches that such esters are useful for stabilizing
06 polypropylene and other organic material normally subject to
07 oxidative deterioration. Similar alkyl esters containing
08 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.
09 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

10
11 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet
12 et al., discloses alkyl esters of hydroxyphenyl carboxylic
13 acids wherein the ester moiety may contain up to 23 carbon
14 atoms. This patent teaches that such compounds are useful
15 as antioxidants for stabilizing emulsion-polymerized
16 polymers.

17
18 It has now been discovered that certain polyalkyl
19 hydroxyaromatic esters provide excellent control of engine
20 deposits, especially intake valve deposits, when employed as
21 fuel additives in fuel compositions. Moreover, these
22 polyalkyl hydroxyaromatic esters have been found to produce
23 fewer combustion chamber deposits than known aliphatic
24 hydrocarbon-substituted phenolic fuel additives.

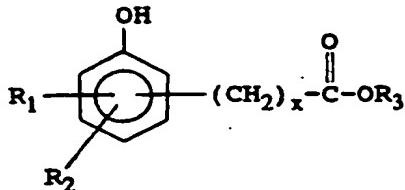
25
26 SUMMARY OF THE INVENTION

27
28 The present invention provides novel polyalkyl
29 hydroxyaromatic esters which are useful as fuel additives
30 for the prevention and control of engine deposits,
31 particularly intake valve deposits.

32
33 The polyalkyl hydroxyaromatic esters of the present
34 invention have the formula:

-5-

01



(I)

02

03

04

05

06

07

or a fuel-soluble salt thereof; wherein R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10.

14

The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a polyalkyl hydroxyaromatic ester of the present invention.

20

The present invention additionally provides a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 150°F to 400°F and from about 10 to 70 weight percent of a polyalkyl hydroxyaromatic ester of the present invention.

26

Among other factors, the present invention is based on the surprising discovery that certain polyalkyl hydroxyaromatic esters, when employed as fuel additives in fuel compositions, provide excellent control of engine deposits, especially on intake valves, and produce fewer combustion chamber deposits than known aliphatic hydrocarbon-substituted phenolic fuel additives.

34

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01

DETAILED DESCRIPTION OF THE INVENTION

02

03 The fuel additives provided by the present invention have
04 the general formula:

05

06



07

08

09

10

11

12

13 or a fuel-soluble salt thereof; wherein R₁, R₂, R₃, and x
14 are as defined hereinabove.

15

16 Preferably, R₁ is hydrogen, hydroxy, or lower alkyl having 1
17 to 4 carbon atoms. More preferably, R₁ is hydrogen or
18 hydroxy. Most preferably, R₁ is hydrogen.

19

20 R₂ is preferably hydrogen.

21

22 Preferably, R₃ is a polyalkyl group having a weight average
23 molecular weight in the range of about 500 to 5,000, more
24 preferably about 500 to 3,000, and most preferably about 600
25 to 2,000.

26

27 Preferably, x is an integer from 0 to 2. More preferably,
28 x is 0.

29

30 A preferred group of polyalkyl hydroxyaromatic esters are
31 those of formula I wherein R₁ is hydrogen, hydroxy, or lower
32 alkyl having 1 to 4 carbon atoms; R₂ is hydrogen; and x
33 is 0.

34

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01 Another preferred group of polyalkyl hydroxyaromatic esters
02 are those of formula I wherein R₁ is hydrogen, hydroxy, or
03 lower alkyl having 1 to 4 carbon atoms; R₂ is hydrogen; and
04 x is 1 or 2.
05

06 A more preferred group of polyalkyl hydroxyaromatic esters
07 are those of formula I wherein R₁ is hydrogen or hydroxy; R₂
08 is hydrogen; and x is 0.
09

10 It is especially preferred that the aromatic hydroxyl group
11 or groups present in the polyalkyl hydroxyaromatic esters of
12 this invention be situated in a meta or para position
13 relative to the polyalkyl ester moiety. When the aromatic
14 moiety contains one hydroxyl group, it is particularly
15 preferred that this hydroxyl group be in a para position
16 relative to the polyalkyl ester moiety.
17

18 The polyalkyl hydroxyaromatic esters of the present
19 invention will generally have a sufficient molecular weight
20 so as to be non-volatile at normal engine intake valve
21 operating temperatures (about 200-250°C). Typically, the
22 molecular weight of the polyalkyl hydroxyaromatic esters of
23 this invention will range from about 600 to about 6,000,
24 preferably from 600 to 3,000, more preferably from 700 to
25 2,000.
26

27 Fuel-soluble salts of the polyalkyl hydroxyaromatic esters
28 of the present invention are also contemplated to be useful
29 for preventing or controlling deposits. Such salts include
30 alkali metal, alkaline earth metal, ammonium, substituted
31 ammonium and sulfonium salts. Preferred metal salts are the
32 alkali metal salts, particularly the sodium and potassium
33 salts, and the substituted ammonium salts, particularly
34

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01 tetraalkyl-substituted ammonium salts, such as the
02 tetrabutylammonium salts.

03

04 Definitions

05

06 As used herein, the following terms have the following
07 meanings unless expressly stated to the contrary.

08

09 The term "alkyl" refers to both straight- and branched-chain
10 alkyl groups.

11

12 The term "lower alkyl" refers to alkyl groups having 1 to
13 about 6 carbon atoms and includes primary, secondary and
14 tertiary alkyl groups. Typical lower alkyl groups include,
15 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
16 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

17

18 The term "lower alkoxy" refers to the group -OR_a wherein R_a
19 is lower alkyl. Typical lower alkoxy groups include
20 methoxy, ethoxy, and the like.

21

22 The term "polyalkyl" refers to alkyl groups which are
23 generally derived from polyolefins which are polymers or
24 copolymers of mono-olefins, particularly 1-mono-olefins,
25 such as ethylene, propylene, butylene, and the like.
26 Preferably, the mono-olefin employed will have 2 to about
27 24 carbon atoms, and more preferably, about 3 to 12 carbon
28 atoms. More preferred mono-olefins include propylene,
29 butylene, particularly isobutylene, 1-octene and 1-decene.
30 Polyolefins prepared from such mono-olefins include
31 polypropylene, polybutene, especially polyisobutene, and the
32 polyalphaolefins produced from 1-octene and 1-decene.

33

34

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01 General Synthetic Procedures

02

03 The polyalkyl hydroxyaromatic esters of this invention may
04 be prepared by the following general methods and procedures.
05 It should be appreciated that where typical or preferred
06 process conditions (e.g., reaction temperatures, times, mole
07 ratios of reactants, solvents, pressures, etc.) are given,
08 other process conditions may also be used unless otherwise
09 stated. Optimum reaction conditions may vary with the
10 particular reactants or solvents used, but such conditions
11 can be determined by one skilled in the art by routine
12 optimization procedures.

13

14 Moreover, those skilled in the art will recognize that it
15 may be necessary to block or protect certain functional
16 groups while conducting the following synthetic procedures.
17 In such cases, the protecting group will serve to protect
18 the functional group from undesired reactions or to block
19 its undesired reaction with other functional groups or with
20 the reagents used to carry out the desired chemical
21 transformations. The proper choice of a protecting group
22 for a particular functional group will be readily apparent
23 to one skilled in the art. Various protecting groups and
24 their introduction and removal are described, for example,
25 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
26 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
27 and references cited therein.

28

29 In the present synthetic procedures, a hydroxyl group will
30 preferably be protected, when necessary, as the benzyl or
31 *tert*-butyldimethylsilyl ether. Introduction and removal of
32 these protecting groups is well described in the art.

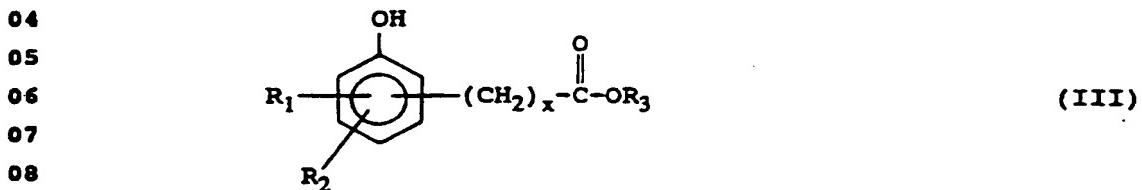
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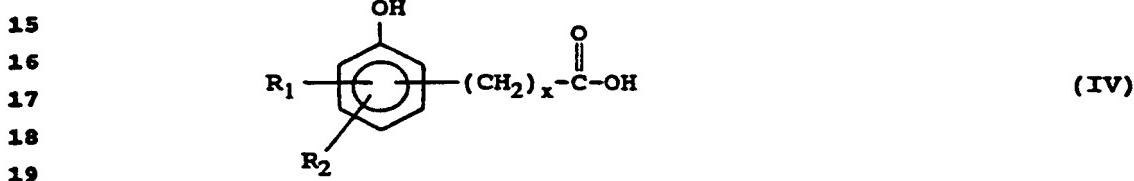
01 The polyalkyl hydroxyaromatic esters of the present
02 invention having the formula:

03



10 wherein R₁, R₂, R₃ and x are as defined above, may be
11 prepared by esterifying a hydroxyaromatic carboxylic acid
12 having the formula:

13



20 wherein R₁, R₂, and x are as defined above, with a polyalkyl
21 alcohol having the formula:

22



26 wherein R₃ is as defined above, using conventional
27 esterification reaction conditions.

28

29 The hydroxyaromatic carboxylic acids of formula IV are
30 either known compounds or can be prepared from known
31 compounds by conventional procedures. Suitable
32 hydroxyaromatic carboxylic acids for use as starting
33 materials in this invention are 2-hydroxybenzoic acid,
34

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01 3-hydroxybenzoic acid, 4-hydroxybenzoic acid,
02 3,4-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid,
03 3-hydroxy-4-methoxybenzoic acid, 4-hydroxy-3-methoxybenzoic
04 acid, 3-t-butyl-4-hydroxybenzoic acid, 3,5-di-t-butyl-4-
05 hydroxybenzoic acid, 4-hydroxyphenylacetic acid,
06 3-(4-hydroxyphenyl)propionic acid and the like.

07

08 The polyalkyl alcohols of formula V may also be prepared by
09 conventional procedures known in the art. Such procedures
10 are taught, for example, in U.S. Patent Nos. 5,055,607 to
11 Buckley and 4,859,210 to Franz et al., the disclosures of
12 which are incorporated herein by reference.

13 15 5

14 In general, the polyalkyl substituent on the polyalkyl
15 alcohols of Formula V and the resulting polyalkyl
16 hydroxyaromatic esters of the present invention will have a
17 weight average molecular weight in the range of about 450 to
18 5,000, preferably about 500 to 5,000, more preferably about
19 500 to 3,000, and most preferably about 600 to 2,000.

20

21 The polyalkyl substituent on the polyalkyl alcohols employed
22 in the invention may be generally derived from polyolefins
23 which are polymers or copolymers of mono-olefins,
24 particularly 1-mono-olefins, such as ethylene, propylene,
25 butylene, and the like. Preferably, the mono-olefin
26 employed will have 2 to about 24 carbon atoms, and more
27 preferably, about 3 to 12 carbon atoms. More preferred
28 mono-olefins include propylene, butylene, particularly
29 isobutylene, 1-octene and 1-decene. Polyolefins prepared
30 from such mono-olefins include polypropylene, polybutene,
31 especially polyisobutene, and the polyalphaolefins produced
32 from 1-octene and 1-decene.

33

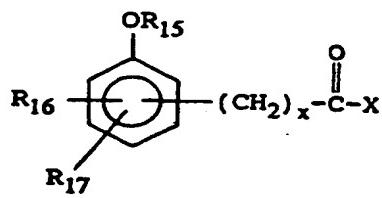
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01 The preferred polyisobutenes used to prepare the presently
02 employed polyalkyl alcohols are polyisobutenes which
03 comprise at least about 20% of the more reactive
04 methylvinylidene isomer, preferably at least 50% and more
05 preferably at least 70%. Suitable polyisobutenes include
06 those prepared using BF_3 catalysts. The preparation of such
07 polyisobutenes in which the methylvinylidene isomer
08 comprises a high percentage of the total composition is
09 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such
10 polyisobutenes, known as "reactive" polyisobutenes, yield
11 high molecular weight alcohols in which the hydroxyl group
12 is at or near the end of the hydrocarbon chain.
13
14 Examples of suitable polyisobutenes having a high
15 alkylvinylidene content include Ultravis 30, a polyisobutene
16 having a molecular weight of about 1300 and a
17 methylvinylidene content of about 74%, and Ultravis 10, a
18 polyisobutene having a molecular weight of about 950 and a
19 methylvinylidene content of about 76%, both available from
20 British Petroleum.
21
22 The polyalkyl alcohols may be prepared from the
23 corresponding olefins by conventional procedures. Such
24 procedures include hydration of the double bond to give an
25 alcohol. Suitable procedures for preparing such long-chain
26 alcohols are described in I. T. Harrison and S. Harrison,
27 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,
28 New York (1971), pp. 119-122, as well as in U.S. Patent
29 Nos. 5,055,607 and 4,859,210.
30
31 As indicated above, the polyalkyl hydroxyaromatic esters of
32 formula III may be prepared by esterifying a hydroxyaromatic
33 carboxylic acid of formula IV with a polyalkyl alcohol of
34

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01 formula V under conventional esterification reaction
 02 conditions.
 03
 04 Typically, this reaction will be conducted by contacting a
 05 polyalkyl alcohol of formula V with about 0.25 to about 1.5
 06 molar equivalents of a hydroxyaromatic carboxylic acid of
 07 formula IV in the presence of an acidic catalyst at a
 08 temperature in the range of about 70°C to about 160°C for
 09 about 0.5 to about 48 hours. Suitable acid catalysts for
 10 this reaction include p-toluene sulfonic acid,
 11 methanesulfonic acid and the like. The reaction may be
 12 conducted in the presence or absence of an inert solvent,
 13 such as benzene, toluene and the like. The water generated
 14 by this reaction is preferably removed during the course of
 15 the reaction by, for example, azeotropic distillation with
 16 an inert solvent, such as toluene.
 17
 18 The polyalkyl hydroxyaromatic esters of formula III may also
 19 be synthesized by reacting a polyalkyl alcohol of formula V
 20 with an acyl halide having the formula:
 21

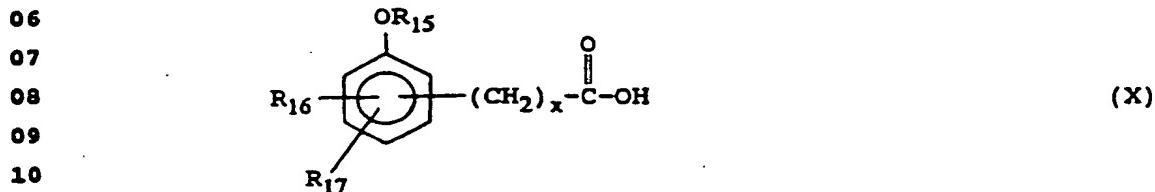


28 wherein X is a halide, such as chloride or bromide, and R₁₅
 29 is a suitable hydroxyl protecting group, such as benzyl,
 30 tert-butyldimethylsilyl, methoxymethyl, and the like; R₁₆
 31 and R₁₇ are each independently hydrogen, lower alkyl, lower
 32 alkoxy, or the group -OR₁₈, wherein R₁₈ is a suitable
 33 hydroxyl protecting group.

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01 Acyl halides of formula IX may be prepared from the
02 hydroxyaromatic carboxylic acids of formula IV by first
03 protecting the aromatic hydroxyl groups of formula IV to
04 form a carboxylic acid having the formula:

05



wherein R₁₅-R₁₇ and x are as defined above, and then
converting the carboxylic acid moiety of formula X into an
acyl halide using conventional procedures.

Protection of the aromatic hydroxyl groups of formula IV may
be accomplished using well known procedures. The choice of
a suitable protecting group for a particular hydroxyaromatic
carboxylic acid will be apparent to those skilled in the
art. Various protecting groups, and their introduction and
removal, are described, for example, in T. W. Greene and
P. G. M. Wuts, *Protective Groups in Organic Synthesis*,
Second Edition, Wiley, New York, 1991, and references cited
therein. Alternatively, the protected derivatives of
formula X can be prepared from known starting materials
other than the hydroxyaromatic compounds of formula IV by
conventional procedures.

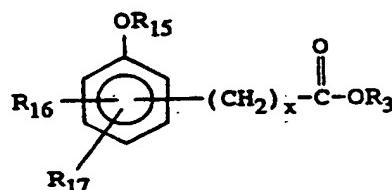
The carboxylic acid moiety of formula X may be converted
into an acyl halide by contacting a compound of formula X
with an inorganic acid halide, such as thionyl chloride,
phosphorous trichloride, phosphorous tribromide, or
phosphorous pentachloride; or alternatively, with oxalyl

-15-

01 chloride. Generally, this reaction will be conducted using
02 about 1 to 5 molar equivalents of the inorganic acid halide
03 or oxalyl chloride, either neat or in an inert solvent, such
04 as diethyl ether, at a temperature in the range of about
05 20°C to about 80°C for about 1 to about 48 hours. A
06 catalyst, such as N,N-dimethylformamide, may also be used in
07 this reaction.

08
09 In certain cases where the hydroxyaromatic carboxylic acids
10 of formula IV having bulky alkyl groups adjacent to the
11 hydroxyl group, such as 3,5-di-t-butyl-4-hydroxybenzoic
12 acid, it will generally not be necessary to protect the
13 hydroxyl group prior to formation of the acyl halide, since
14 such hydroxyl groups are sufficiently sterically hindered so
15 as to be substantially non-reactive with the acyl halide
16 moiety.

17
18 Reaction of an acyl halide of formula IX with a polyalkyl
19 alcohol of formula V provides an intermediate polyalkyl
20 ester having the formula:



28 wherein R₃, R₁₅-R₁₇, and x are as defined above.
29

30
31 Typically, this reaction is conducted by contacting an
32 alcohol of formula V with about 0.9 to about 1.5 molar
33 equivalents of an acyl halide of formula IX in an inert
34 solvent, such as toluene, dichloromethane, diethyl ether,

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01 and the like, at a temperature in the range of about 25°C to
02 about 150°C. The reaction is generally complete in about
03 0.5 to about 48 hours. Preferably, the reaction is
04 conducted in the presence of a sufficient amount of an amine
05 capable of neutralizing the acid generated during the
06 reaction, such as triethylamine, di(isopropyl)ethylamine,
07 pyridine or 4-dimethylamino-pyridine.

08
09 Deprotection of the aromatic hydroxyl group(s) on the esters
10 of formula XI then provides a polyalkyl hydroxyaromatic
11 ester of formula III. Appropriate conditions for this
12 deprotection step will depend upon the protecting group(s)
13 utilized in the synthesis and will be readily apparent to
14 those skilled in the art. For example, benzyl protecting
15 groups may be removed by hydrogenolysis under 1 to about 4
16 atmospheres of hydrogen in the presence of a catalyst, such
17 as palladium on carbon. Typically, this deprotection
18 reaction is conducted in an inert solvent, preferably a
19 mixture of ethyl acetate and acetic acid, at a temperature
20 of from about 0°C to about 40°C for about 1 to about
21 24 hours.

22

23 Fuel Compositions

24

25 The polyalkyl hydroxyaromatic esters of the present
26 invention are useful as additives in hydrocarbon fuels to
27 prevent and control engine deposits, particularly intake
28 valve deposits. The proper concentration of additive
29 necessary to achieve the desired deposit control varies
30 depending upon the type of fuel employed, the type of
31 engine, and the presence of other fuel additives.

32

33 In general, the concentration of the polyalkyl
34 hydroxyaromatic esters of this invention in hydrocarbon fuel

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01 will range from about 50 to about 2500 parts per million
02 (ppm) by weight, preferably from 75 to 1,000 ppm. When
03 other deposit control additives are present, a lesser amount
04 of the present additive may be used.
05

06 The polyalkyl hydroxyaromatic esters of the present
07 invention may be formulated as a concentrate using an inert
08 stable oleophilic (i.e., dissolves in gasoline) organic
09 solvent boiling in the range of about 150°F to 400°F (about
10 65°C to 205°C). Preferably, an aliphatic or an aromatic
11 hydrocarbon solvent is used, such as benzene, toluene,
12 xylene or higher-boiling aromatics or aromatic thinners.
13 Aliphatic alcohols containing about 3 to 8 carbon atoms,
14 such as isopropanol, isobutylcarbinol, n-butanol and the
15 like, in combination with hydrocarbon solvents are also
16 suitable for use with the present additives. In the
17 concentrate, the amount of the additive will generally range
18 from about 10 to about 70 weight percent, preferably 10 to
19 50 weight percent, more preferably from 20 to 40 weight
20 percent.
21

22 In gasoline fuels, other fuel additives may be employed with
23 the additives of the present invention, including, for
24 example, oxygenates, such as t-butyl methyl ether, antiknock
25 agents, such as methylcyclopentadienyl manganese
26 tricarbonyl, and other dispersants/detergents, such as
27 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
28 succinimides. Additionally, antioxidants, metal
29 deactivators and demulsifiers may be present.
30

31 In diesel fuels, other well-known additives can be employed,
32 such as pour point depressants, flow improvers, cetane
33 improvers, and the like.
34

-18-

01 A fuel-soluble, nonvolatile carrier fluid or oil may also be
02 used with the polyalkyl hydroxyaromatic esters of this
03 invention. The carrier fluid is a chemically inert
04 hydrocarbon-soluble liquid vehicle which substantially
05 increases the nonvolatile residue (NVR), or solvent-free
06 liquid fraction of the fuel additive composition while not
07 overwhelmingly contributing to octane requirement increase.
08 The carrier fluid may be a natural or synthetic oil, such as
09 mineral oil, refined petroleum oils, synthetic polyalkanes
10 and alkenes, including hydrogenated and unhydrogenated
11 polyalphaolefins, and synthetic polyoxyalkylene-derived
12 oils, such as those described, for example, in U.S. Patent
13 No. 4,191,537 to Lewis, and polyesters, such as those
14 described, for example, in U.S. Patent Nos. 3,756,793 and
15 5,004,478 to Robinson and Vogel et al., respectively, and in
16 European Patent Application Nos. 356,726 and 382,159,
17 published March 7, 1990 and August 16, 1990, respectively.
18
19 These carrier fluids are believed to act as a carrier for
20 the fuel additives of the present invention and to assist in
21 removing and retarding deposits. The carrier fluid may also
22 exhibit synergistic deposit control properties when used in
23 combination with a hydroxyaromatic polyalkyl compound of
24 this invention.
25
26 The carrier fluids are typically employed in amounts ranging
27 from about 100 to about 5000 ppm by weight of the
28 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
29 fuel. Preferably, the ratio of carrier fluid to deposit
30 control additive will range from about 0.5:1 to about 10:1,
31 more preferably from 1:1 to 4:1, most preferably about 2:1.
32
33 When employed in a fuel concentrate, carrier fluids will
34 generally be present in amounts ranging from about 20 to

-19-

01 about 60 weight percent, preferably from 30 to 50 weight
02 percent.

03

EXAMPLES

05

06 The following examples are presented to illustrate specific
07 embodiments of the present invention and synthetic
08 preparations thereof; and should not be interpreted as
09 limitations upon the scope of the invention.

10

Example 1

11

Preparation of Polyisobutyl 4-Hydroxybenzoate

12

13 To a flask equipped with a mechanical stirrer, thermometer,
14 Dean Stark trap, reflux condensor and nitrogen inlet was
15 added 525 grams of polyisobutanol (molecular weight average
16 984, prepared via hydroformylation of Amoco H-100
17 polyisobutene), 124.7 grams of 4-hydroxybenzoic acid, and
18 13.0 grams of p-toluene sulfonic acid. The mixture was
19 stirred at 130°C for sixteen hours, cooled to room
20 temperature and diluted with 2 liters of diethyl ether. The
21 organic phase was washed two times with saturated aqueous
22 sodium bicarbonate, once with brine, dried over anhydrous
23 magnesium sulfate, filtered and concentrated in vacuo to
24 yield 514.3 grams of the desired product as a yellow oil.
25 IR (neat) 1715, 1685 cm⁻¹; ¹H NMR (CDCl₃) δ 7.95 (d, 2H), 6.9
26 (d, 2H), 5.8 (bs, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).

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-20-

01

Example 2

02

03

Preparation of Polyisobutyl 4-Hydroxyphenylacetate

04

05 To a flask equipped with a mechanical stirrer, thermometer,
06 Dean Stark trap, reflux condensor and nitrogen inlet was
07 added 35.0 grams of polyisobutanol (molecular weight average
08 984, prepared via hydroformylation of Amoco H-100
09 polyisobutene), 9.16 grams of 4-hydroxyphenylacetic acid,
10 and 0.86 grams of p-toluene sulfonic acid. The mixture was
11 stirred at 130°C for sixteen hours, cooled to room
12 temperature and diluted with 500 milliliters of diethyl
13 ether. The organic phase was washed three times with
14 methanol/water (4:1), once with brine, dried over anhydrous
15 magnesium sulfate, filtered and concentrated in vacuo to
16 yield 45.8 grams of a brown oil. The oil was
17 chromatographed on silica gel eluting with hexane/ethyl
18 acetate/ethanol (8:1.8:0.2) to yield 26.6 grams of the
19 desired product as a yellow oil. IR (neat) 1714 cm⁻¹; ¹H NMR
20 (CDCl₃) δ 7.15 (d, 2H), 6.75 (d, 2H), 5.05 (bs, 1H), 4.1
21 (t, 2H), 3.5 (s, 2H), 0.6-1.8 (m, 137H).

22

23

Example 3

24

25

Preparation of Polyisobutyl Salicylate

26

27

28 To a flask equipped with a mechanical stirrer, thermometer,
29 Dean Stark trap, reflux condensor and nitrogen inlet was
30 added 35.0 grams of polyisobutanol (molecular weight average
31 984, prepared via hydroformylation of Amoco H-100
32 polyisobutene), 8.3 grams of salicylic acid, and 0.86 grams
33 of p-toluene sulfonic acid. The mixture was stirred at
34 130°C for sixteen hours, cooled to room temperature and

-21-

01 diluted with 500 milliliters of diethyl ether. The organic
02 phase was washed three times with methanol/water (4:1), once
03 with brine, dried over anhydrous magnesium sulfate, filtered
04 and concentrated in vacuo to yield 43.3 grams of a yellow
05 oil. The oil was chromatographed on silica gel eluting with
06 hexane/ethyl acetate/ethanol (8:1.8:0.2) to yield 26.4 grams
07 of the desired product as a yellow oil. IR (neat)
08 1682 cm⁻¹; ¹H NMR (CDCl₃) δ 10.8 (s, 1H), 7.8 (d, 1H), 7.4
09 (t, 1H), 7.0 (d, 1H), 6.8 (t, 1H), 4.3 (t, 2H), 0.6-1.8 (m,
10 137H).

11

Example 4

12

Preparation of 4-Benzylxy-2,6-dimethylbenzoyl Chloride

13

14 To a flask equipped with a magnetic stirrer and nitrogen
15 inlet was added 11.35 grams of 4-benzylxy-2,6-
16 dimethylbenzoic acid (prepared as described by S. Thea,
17 G. Cevasco, G. Guanti, N. Kashefi-Naini and A. Williams,
18 J. Org. Chem., 50, 1867 (1985)), 120 mL of anhydrous
19 methylene chloride, followed by 9.7 mL of oxalyl chloride.
20 The resulting mixture was stirred at room temperature for
21 16 hours and then the solvent was removed in vacuo to yield
22 11.4 grams of the desired acid chloride.

23

24

Example 5

25

Preparation of Polyisobutyl 4-Benzylxy-2,6-dimethylbenzoate

26

27

28 4-Benzylxy-2,6-dimethylbenzoyl chloride (5.3 grams) from
29 Example 4 was combined with 13.5 grams of polyisobutanol
30 (molecular weight average 984, prepared via hydroformylation
31 of Amoco H-100 polyisobutene) and 200 mL of anhydrous

32

33

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-22-

01 toluene. Triethylamine (2.8 mL) and 4-dimethylaminopyridine
02 (1.18 grams) were then added and the resulting mixture was
03 heated to reflux under nitrogen for 16 hours. The reaction
04 was cooled to room temperature and diluted with diethyl
05 ether. The organic layer was washed twice with 1% aqueous
06 hydrochloric acid, twice with saturated aqueous sodium
07 bicarbonate solution, and once with brine. The organic
08 layer was then dried over anhydrous magnesium sulfate,
09 filtered and the solvents removed *in vacuo* to yield
10 17.8 grams of a brown oil. The oil was chromatographed on
11 silica gel, eluting with hexane/ethyl acetate/ethanol
12 (9:0.8:0.2), to yield 16.8 grams of the desired product as a
13 brown oil.

14

15

Example 6

16

17

Preparation of Polyisobutyl 4-Hydroxy-2,6-dimethylbenzoate

18

19

A solution of 16.8 grams of the product from Example 5 in
20 100 mL of ethylacetate and 100 mL of acetic acid containing
21 3.0 grams of 10% palladium on charcoal was hydrogenolyzed at
22 35-40 psi for 16 hours on a Parr low-pressure hydrogenator.
23 Catalyst filtration and removal of residual acetic acid with
24 toluene *in vacuo* yielded 13.6 grams of the desired product
25 as a yellow oil. IR (neat) 1729, 1696 cm^{-1} ; ^1H NMR (CDCl_3) δ
26 6.5 (s, 2H), 5.0 (bs, 1H), 4.3 (t, 2H), 2.3 (s, 6H), 0.6-1.8
27 (m, 137H).

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-23-

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Example 7

02

03

Preparation of Polyisobutanol via Hydroboration

04

05

Polyisobutene (molecular weight average 700, available from Exxon as Parapol 700, 100 grams) was combined with anhydrous tetrahydrofuran (1.0 L) and cooled to 0°C under nitrogen. Borane-tetrahydrofuran complex (157 mL of a 1 M solution of borane in tetrahydrofuran) was added dropwise and then the reaction was allowed to warm to room temperature and stirred for sixteen hours. 143 mL of 3 N aqueous sodium hydroxide was added dropwise followed by 52.5 mL of 30% aqueous hydrogen peroxide. The mixture was stirred at room temperature for one hour and then diluted with 2.0 L of diethyl ether. The organic phase was washed three times with water, once with brine, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 96.4 grams of a yellow oil. The oil was chromatographed on silica gel eluting with hexane followed by hexane/ethyl acetate/ethanol (9:0.8:0.2) to yield 91 grams of the desired product as a light yellow oil.

22

23

Example 8

24

25

Preparation of 4-Benzylxybenzoyl Chloride

26

27

To a flash equipped with a magnetic stirrer and drying tube was added 75.0 grams of 4-benzylxybenzoic acid and 700 mL of anhydrous methylene chloride and then 72 mL of oxalyl chloride. The resulting mixture was stirred at room temperature for 16 hours and then the solvent was removed in vacuo to yield 79.6 grams of the desired acid chloride.

33

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-24-

Example 9

Preparation of Polyisobutyl 4-Benzoyloxybenzoate

05 4-Benzylxybenzoyl chloride (6.9 grams) from Example 8 was
06 combined with 20.0 grams of polyisobutanol from Example 7
07 and 200 mL of toluene. Triethylamine (4.1 mL) and
08 4-dimethylaminopyridine (1.70 grams) were then added and the
09 resulting mixture was heated to reflux for 16 hours. The
10 reaction was cooled to room temperature and diluted with
11 diethyl ether. The organic layer was washed twice with 1%
12 aqueous hydrochloric acid, twice with saturated aqueous sodium
13 bicarbonate solution, and once with brine. The organic
14 layer was then dried over anhydrous magnesium sulfate,
15 filtered and the solvents removed in vacuo to yield
16 24.9 grams of a yellow oil. The oil was chromatographed on
17 silica gel eluting with hexane/diethyl ether/ethanol
18 (9:0.8:0.2), to yield 20.6 grams of the desired product as a
19 light yellow oil.

31 Example 10

**Preparation of Polyisobutyl 4-Hydroxybenzoate
from Hydroborated Polyisobutene**

26 A solution of 20.6 grams of the product from Example 9 in
 27 100 mL of ethylacetate and 100 mL of acetic acid containing
 28 3.0 grams of 10% palladium on charcoal was hydrogenolyzed at
 29 35-40 psi for 16 hours on a Parr low-pressure hydrogenator.
 30 Catalyst filtration and removal of residual acetic acid with
 31 toluene in vacuo yielded 19.2 grams of the desired product
 32 as a light yellow oil. IR (neat) 1716, 1682 cm⁻¹; ¹H NMR

-25-

01 (CDCl_3) δ 8.0 (d, 2H), 6.9 (d, 2H), 5.1 (m, 1H), 0.6-1.8
02 (m, 96H).

03

04 Example 11

05

06 Single-Cylinder Engine Test

07

08 The test compounds were blended in gasoline and their
09 deposit reducing capacity determined in an ASTM/CFR
10 single-cylinder engine test.

11

12 A Waukesha CFR single-cylinder engine was used. Each run
13 was carried out for 15 hours, at the end of which time the
14 intake valve was removed, washed with hexane and weighed.
15 The previously determined weight of the clean valve was
16 subtracted from the weight of the valve at the end of the
17 run. The differences between the two weights is the weight
18 of the deposit. A lesser amount of deposit indicates a
19 superior additive. The operating conditions of the test
20 were as follows: water jacket temperature 200°F; vacuum of
21 12 in Hg, air-fuel ratio of 12, ignition spark timing of
22 40° BTC; engine speed is 1800 rpm; the crankcase oil is a
23 commercial 30W oil.

24

25 The amount of carbonaceous deposit in milligrams on the
26 intake valves is reported for each of the test compounds in
27 Table I and Table II.

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-26-

TABLE I

Sample ¹	Intake Valve Deposit Weight (in milligrams)		
	Run 1	Run 2	Average
Base Fuel	164.4	158.1	161.3
Example 1	27.0	35.0	31.0
Example 6	17.2	12.2	14.7
Example 10	7.0	7.6	7.3

¹At 200 parts per million actives (ppma).TABLE II

Sample ¹	Intake Valve Deposit Weight (in milligrams)		
	Run 1	Run 2	Average
Base Fuel	302.6	312.2	307.4
Example 2	68.9	57.4	63.2
Example 3	272.0	232.7	252.4

¹At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table I and Table II illustrates the significant reduction in intake valve deposits provided by the polyalkyl hydroxyaromatic esters of the present invention (Examples 1, 2, 3, 6 and 10) compared to the base fuel.

-27-

01

Example 12

02

Multicylinder Engine Test

03

04
05 The polyalkyl hydroxyaromatic esters of the present
06 invention were tested in a laboratory multicylinder engine
07 to evaluate their intake valve and combustion chamber
08 deposit control performance. The test engine was a
09 4.3 liter, TBI (throttle body injected), V6 engine
10 manufactured by General Motors Corporation.

11

12 The major engine dimensions are set forth in Table III:

13

Table III

14

Engine Dimensions

15

16

17

Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

18

19 The test engine was operated for 40 hours (24 hours a day)
20 on a prescribed load and speed schedule representative of
21 typical driving conditions. The cycle for engine operation
22 during the test is set forth in Table IV.

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-28-

01

Table IV

02

03

Engine Driving Cycle

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Step	Mode	Time in Mode [Sec] ¹	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

¹ All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table V.

-29-

01

Table V

02

Multicylinder Engine Test Results

03

04

05

06

07

08

09

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12

Sample ¹		Intake Valve Deposits ²	Combustion Chamber Deposits ²
Base Fuel	Run 1	710	2339
	Run 2	962	2059
	Average	836	2199
Example 1	Run 1	238	2317
	Run 2	292	2418
	Average	265	2368

13

¹At 200 parts per million actives (ppma).

14

²In milligrams (mg).

15

16

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

21

The data in Table V illustrates the significant reduction in intake valve deposits provided by the polyalkyl hydroxyaromatic esters of the present invention (Example 1) compared to the base fuel. Moreover, the data in Table V further demonstrates that the polyalkyl hydroxyaromatic esters of the present invention do not contribute significantly to combustion chamber deposits.

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01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

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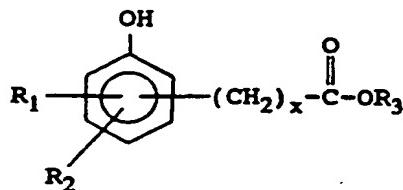
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22

23 2. The compound according to Claim 1, wherein R₁ is

24 hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon

atoms; and R₂ is hydrogen.

25

26 3. The compound according to Claim 2, wherein R₁ is

27 hydrogen or hydroxy.

28

29 4. The compound according to Claim 1, wherein x is 0, 1 or

30 2.

31

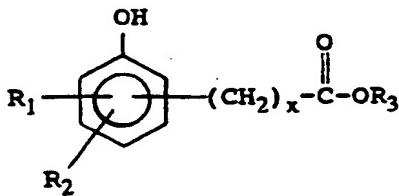
32 5. The compound according to Claim 4, wherein R₁ and R₂

33 are hydrogen, and x is 0.

34

-31-

- 01 6. The compound according to Claim 1, wherein R₃ is a
02 polyalkyl group having a weight average molecular
03 weight in the range of about 500 to 5,000.
- 04
- 05 7. The compound according to Claim 6, wherein R₃ has a
06 weight average molecular weight in the range of about
07 500 to 3,000.
- 08
- 09 8. The compound according to Claim 7, wherein R₃ has a
10 weight average molecular weight in the range of about
11 600 to 2,000.
- 12
- 13 9. The compound according to Claim 1, wherein R₃ is a
14 polyalkyl group derived from polypropylene, polybutene,
15 or polyalphaolefin oligomers of 1-octene or 1-decene.
- 16
- 17 10. The compound according to Claim 9, wherein R₃ is
18 derived from polyisobutene.
- 19
- 20 11. The compound according to Claim 10, wherein the
21 polyisobutene contains at least about 20% of a
22 methylvinylidene isomer.
- 23
- 24 12. A fuel composition comprising a major amount of
25 hydrocarbons boiling in the gasoline or diesel range
26 and an effective detergent amount of a compound of the
27 formula:
- 28

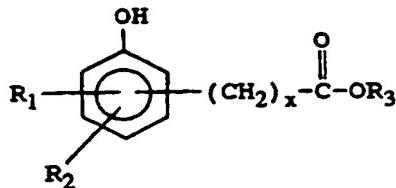


-32-

- 01 or a fuel-soluble salt thereof; wherein
02
03 R₁ and R₂ are independently hydrogen, hydroxy, lower
04 alkyl having 1 to 6 carbon atoms, or lower alkoxy
05 having 1 to 6 carbon atoms;
06
07 R₃ is a polyalkyl group having a weight average
08 molecular weight in the range of about 450 to 5,000;
09 and x is an integer from 0 to 10.
10
11 13. The fuel composition according to Claim 12, wherein R₁
12 is hydrogen, hydroxy, or lower alkyl having 1 to 4
13 carbon atoms and R₂ is hydrogen.
14
15 14. The fuel composition according to Claim 13, wherein R₁
16 is hydrogen or hydroxy.
17
18 15. The fuel composition according to Claim 12, wherein x
19 is 0, 1 or 2.
20
21 16. The fuel composition according to Claim 15, wherein R₁
22 and R₂ are hydrogen, and x is 0.
23
24 17. The fuel composition according to Claim 12, wherein R₃
25 is a polyalkyl group having a weight average molecular
26 weight in the range of about 500 to 5,000.
27
28 18. The fuel composition according to Claim 17, wherein R₃
29 has a weight average molecular weight in the range of
30 about 500 to 3,000.
31
32
33
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-33-

- 01 19. The fuel composition according to Claim 18, wherein R₃
02 has a weight average molecular weight in the range of
03 about 600 to 2,000.
04
05 20. The fuel composition according to Claim 12, wherein R₃
06 is a polyalkyl group derived from polypropylene,
07 polybutene, or polyalphaolefin oligomers of 1-octene or
08 1-decene.
09
10 21. The fuel composition according to Claim 20, wherein R₃
11 is derived from polyisobutene.
12
13 22. The fuel composition according to Claim 21, wherein the
14 polyisobutene contains at least about 20% of a
15 methylvinylidene isomer.
16
17 23. The fuel composition according to Claim 12, wherein
18 said composition contains about 50 to about 2500 parts
19 per million by weight of said compound.
20
21 24. A fuel concentrate comprising an inert stable
22 oleophilic organic solvent boiling in the range of from
23 about 150°F to 400°F and from about 10 to about 70
24 weight percent of a compound of the formula:
25
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34



or a fuel-soluble salt thereof; wherein

-34-

- 01 R₁ and R₂ are independently hydrogen, hydroxy, lower
02 alkyl having 1 to 6 carbon atoms, or lower alkoxy
03 having 1 to 6 carbon atoms;
04
05 R₃ is a polyalkyl group having a weight average
06 molecular weight in the range of about 450 to 5,000;
07 and x is an integer from 0 to 10.
08
09 25. The fuel concentrate according to Claim 24, wherein R₁
10 is hydrogen, hydroxy, or lower alkyl having 1 to 4
11 carbon atoms and R₂ is hydrogen.
12
13 26. The fuel concentrate according to Claim 25, wherein R₁
14 is hydrogen or hydroxy.
15
16 27. The fuel concentrate according to Claim 24, wherein x
17 is 0, 1 or 2.
18
19 28. The fuel concentrate according to Claim 27, wherein R₁
20 and R₂ are hydrogen, and x is 0.
21
22 29. The fuel concentrate according to Claim 24, wherein R₃
23 is a polyalkyl group having a weight average molecular
24 weight in the range of about 500 to 5,000.
25
26 30. The fuel concentrate according to Claim 29, wherein R₃
27 was a weight average molecular weight in the range of
28 about 500 to 3,000.
29
30 31. The fuel concentrate according to Claim 30, wherein R₃
31 has a weight average molecular weight in the range of
32 about 600 to 2,000.
33
34

-35-

- 01 32. The fuel concentrate according to Claim 24, wherein R₃
02 is a polyalkyl group derived from polypropylene,
03 polybutene, or polyalphaolefin oligomers of 1-octene or
04 1-decene.
05
06 33. The fuel concentrate according to Claim 32, wherein R₃
07 is derived from polyisobutene.
08
09 34. The fuel concentrate according to Claim 33, wherein the
10 polyisobutene contains at least about 20% of a
11 methylvinylidene isomer.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/12365

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10L 1/18; C07C 69/76, 88
US CL : 44/400; 560/67, 70, 71, 75

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/400; 560/67, 70, 71, 75

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,713,475 (SPIVACK ET AL.) 15 DECEMBER 1987, column 1, line 56 to column 2, line 4).	1, 4 and 6-8 -----
Y	US, A, 3,330,859 (DEXTER ET AL.) 11 JULY 1967, column 1, lines 14-61.	9-11
Y	US, A, 5,206,414 (EVANS ET AL.) 27 APRIL 1993, column 1, lines 43-68; column 16, lines 13-19; column 20, lines 15-24.	1, 4, 6--24 and 29-34
		1-34

Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
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Date of the actual completion of the international search

31 JANUARY 1995

Date of mailing of the international search report

17 FEB 1995

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